



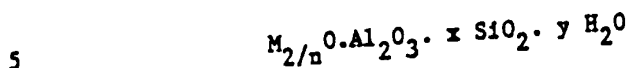
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(54) Title: MODIFICATION OF ZEOLITES (57) Abstract <p>A method for the modification of the framework structure of a zeolite comprises treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework, the aluminium-replacing element being selected from, for example, boron, tin, silicon, titanium, germanium, gallium, phosphorus, beryllium and magnesium preferably in the form of their halides or organometallic compounds. Typical compounds are BCl₃, BBr₃, SnCl₄, SnBr₄, SnI₄, SiCl₄, SiI₄, TiCl₄, GeCl₄, GaCl₃, PCl₃, BeCl₂, MgCl₂ and beryllium diphenyl. In a preferred embodiment the zeolite is reacted with silicon tetrachloride in carbon tetrachloride under reflux. However, the reaction time can be reduced by utilizing a solvent which has a molecular size which prevents it entering the channels of the zeolite, one such solvent being tetraethoxysilane.</p>		

Modification of Zeolites

This invention relates to a process for the chemical modification of zeolite structures.

Zeolites are crystalline hydrated aluminium silicates which have the general chemical formula:

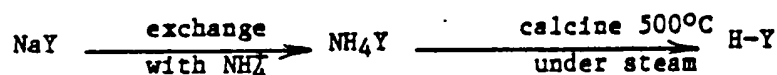


where M is a cation of valency n and x is greater than or equal to 2.0. Structurally they have a porous framework based on an extended three-dimensional framework of SiO_4 and AlO_4 tetrahedra linked together through common oxygen atoms.

10 A large number of natural and synthetic zeolites are known but only a comparative few of these have found application as catalysts in the chemical industry. However, the important catalysts faujasite (in the form of the synthetic-zeolites X and Y), mordenite and ZSM-5 (Trade Mark) are used in substantial
15 quantity: for example, more than 100,000 tons per year in 1970 were consumed in petroleum cracking. It is synthetic faujasite (as zeolite Y) which is principally used for this purpose. However, as synthesised, the value of x in the above formula for zeolite Y is approximately 5.0 and the resulting framework is not
20 sufficiently stable to withstand the high temperatures (800°C) involved in the regenerator unit of cracking plants where coke is burnt off. (By "coke" is meant the deposits of carbon and low hydrogen content hydrocarbons that build up in petroleum cracking). To improve the thermal stability of the zeolite, the
25 SiO_2/Al_2O_3 ratio has to be increased.

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Several methods have been proposed but, principally for reasons of cost, the preferred methods are based on the following chemical process:



5 that is, the hydrogen (H^+) form is made by calcination of the ammonium (NH_4^+) exchanged form in the presence of steam at high temperatures. This results in some of the aluminium atoms leaving the framework and being deposited in the channel network as extra-framework aluminium. The vacancies are filled by atoms
10 of silicon diffusing from other parts of the crystallites. Obviously the net result is the production of a partially crystalline material along with some amorphous material and the introduction of some mesopores into the system. The resulting material, however, is an excellent selective catalyst.

15 The other methods which can be used to increase the silicon to aluminium ratio are (a) extraction of aluminium by EDTA (ethylenediaminetetraacetic acid) (b) acid treatment and (c) use of silicon tetrachloride vapour. EP-A-82211 describes the use of an aqueous solution of a fluorosilicate to replace aluminium with
20 silicon in the framework. The use of the SiCl_4 vapour, as described for example in EP-A-62123 and EP-A-72397, has some useful effects. The vacancies in the framework, produced by the extraction of aluminium, are healed by silicon atoms from the tetrachloride, and, the aluminium removed from the framework is
25 converted to its volatile trichloride effecting removal from the system. However, problems associated with the vapour phase process are (a) the cost of the silicon tetrachloride, (b) the high temperature required, and, (c) the potential danger of collapse of the structure of the framework unless the temperature
30 is strictly controlled.

EP-A-210018 describes another process for the modification of zeolite framework structures which involves treatment of the zeolite with a molten salt medium which contains a reactive component which has a "radius ratio" of less than 0.6, the "radius ratio" being defined as the ratio of the crystal ionic radius of the central atom of the reactive component to that of the oxygen anion O^{2-} . The method is applicable to porous crystalline minerals which have pores large enough to sorb normal hexane. Examples of the components which have the required radius ratio are: the trichlorides of aluminium, boron, iron, phosphorus and gallium, and the tetrachlorides of titanium and tin, the Si^{4+} ion being also mentioned. The method may be used to insert aluminium into high silicon zeolite frameworks or otherwise alter the framework without substantial alteration of its structure.

An object of the present invention is to provide an improved method for the modification of zeolite framework structures.

According to the present invention there is provided a method for the modification of the framework structure of a zeolite comprising treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework.

The compound is preferably a metal halide of the aluminium-replacing element, examples being: BCl_3 , BBr_3 , $SnCl_4$, $SnBr_4$, SnI_4 , $SiCl_4$, SiI_4 , $TiCl_4$, $GeCl_4$, GeI_4 , PCl_5 , $BeCl_2$, $AlCl_3$ and $MgCl_2$. However, organometallic compounds of the selected element may also be suitable, for example, beryllium diphenyl.

The zeolite may be, for example, Erionite, Beta, ZSM-5, ZSM-11 (Trade Marks), Mordenite, Chabazite, and Offretite.

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The selection of the solvent is not critical. Solvents, and solvent mixtures, of small molecular size, such as carbon tetrachloride and ethanol, are suitable but the reaction may be accelerated by the use of a solvent of a molecular size which is too large to enter the channels of the zeolite, one particularly preferred solvent for this purpose being tetraethoxysilane $[\text{C}_2\text{H}_5\text{O}]_4\text{Si}$.

The temperature of the treatment is not of critical importance but would normally be carried out at the reflux temperature of the solvent in order to minimise the treatment time.

The method of the invention may include a pretreatment step in which the zeolite is treated with acid to effect a desired degree of dealumination, prior to treatment with the solvent solution compound of the aluminium-replacing element. Since the degree of dealumination with acid is restricted only by the need to maintain the integrity of the zeolitic structure, the use of the acid pretreatment step enables the production of zeolites with very high silicon to aluminium ratios.

As well as increasing the thermal stability of the zeolite increase of the silicon to aluminium ratio improves the Bronsted activity of the OH groups which remain in the dealuminated framework.

The invention will now be described, by way of illustration, in the following Examples.

25 EXAMPLE 1

About 1 gram of NaY zeolite was calcined in a muffle furnace at 600°C for a few hours. The zeolite was then cooled to $80-100^\circ\text{C}$ in a desiccator and 25ml of carbon tetrachloride (CCl_4) was then added with continuous stirring to form a slurry. Various amounts (0.10 to 0.77ml) of silicon

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tetrachloride (SiCl_4) were added to several separate samples of the slurry which were then refluxed at a fixed temperature (58-59°C; 76-77°C) for a period of three hours. The final slurry was then centrifuged to separate the solid and liquid phases. Three successive portions of CCl_4 (approximately 15ml) followed by three successive portions of ethanol (approximately 15ml) were employed during the solid/liquid separation stage. The product was dried on a water bath and treated with sodium chloride solution (1-5M) repeatedly to convert the zeolite to the pure sodium form. The product was then well washed with distilled deionised water (boiled and cooled out of contact with air) until free of chloride, dried at 100°C and calcined at 600°C for one hour.

The calcined zeolite was allowed to cool and treated with sodium chloride solution (1-5M at pH 8-9) repeatedly. The final product was well washed until chloride-free, filtered and dried at 100°C.

Analysis of the dealuminated samples was as follows:

- (a) Dealuminated samples were calcined at 600°C to obtain the dry weight and the residues dissolved to determine the aluminium content by EDTA titration.
- (b) Sodium was determined by ^{22}Na tracer method.
- (c) Silicon was estimated by difference.
- (d) Collapse temperature was determined by differential thermal analysis using a Du Pont 990 Thermal Analyser (in nitrogen).

The results are reported in Table I below.

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TABLE I

	Sample No.	SiCl ₄ added(ml)	Reflux T°C	Al mmol/g	Na mmol/g	Al /u.c.*	Collapse T°C
5	CS0.10/58	0.10	58-59	2.95	2.92	49.3	1012
	CS0.20/58	0.20	58-59	2.97	2.89	50.1	1014
	CS0.33/58	0.33	58-59	2.79	2.83	46.8	1023
	CS0.40/58	0.40	58-59	2.84	2.86	47.5	1015
	CS0.77/58	0.77	58-59	2.86	2.82	47.3	993
10	CS0.10/76	0.10	76-77	2.98	2.94	49.5	984
	CS0.27/76	0.27	76-77	2.78	2.72	45.8	1009
	CS0.33/76	0.33	76-77	2.71	2.61	45.3	1021
	CS0.77/76	0.77	76-77	2.74	2.64	44.8	1007
Starting Material, NaY				3.28	3.11	56.1	933

* based on total Al present - 192 Al sites in unit cell (u.c.)

15 EXAMPLE 2

The same procedure as described in Example 1 was used except that 15ml of CCl₄ and 0.3ml SiCl₄ were refluxed with NaY zeolite with different water content at 59°C for 20 minutes. The results are given in Table II below.

20

TABLE II

Sample No.	Water content/u.c.	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
CS (1)	11	2.96	2.89	49.9	1002
CS (2)	30	2.90	2.91	48.4	1015
25 CS (3)	23	2.90	2.89	48.7	1013
CS (4)	39	2.90	3.01	48.1	1008
0.3 CSH	245	2.47	2.38	39.8	998

EXAMPLE 3

Using the procedure described in Example 1 above, 20ml of CCl_4 and 10ml SiCl_4 were refluxed with zeolites with different cationic forms at 58-60°C for one hour.

5 The results are given in Table III below.

TABLE III

Sample No.	Cationic form	Al mmol/g	Na/other cation mmol/g	Al /u.c.	Collapse T°C	
10	LiY 600*	Li	3.01	2.66	49.0	1001
	NaY 600	Na	2.70	2.64	44.5	1030
	KY 600	K	2.89	2.71	47.1	1015
	CsY 600	Cs, Na **	3.12	3.11	52.4	996
	BaY 600	Ba, Na **	3.09	2.32	50.0	982
	2LaY 600	La, Na **	2.84	1.71/0.66	52.0	956
	CeY 600	Ce, Na **	2.91	1.77/0.69	53.7	978

* zeolite Y calcined at 600°C

** 16 Na⁺ in small cages.

EXAMPLE 4

20 Using the same procedure as is described in Example 1, 30ml of SiCl_4 was refluxed with NaY zeolite at 57°C and samples were withdrawn after 30, 60 and 90 minutes.

The results are reported in Table IV below.

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TABLE IV

Sample No.	Reflux Time (min)	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
5	S0.50/57 30	2.31	2.24	37.5	1031
	S1.0/57 60	2.33	2.20	37.0	-
	S1.5/57 90	2.32	2.25	37.3	1041
	SS0.5/1.5 30	2.16	1.93	33.2	1070

Samples S0.50/57, S1.0/57 and S1.5/57 were mixed with 15ml SiCl_4 and refluxed at 57°C for 30 minutes to produce sample SS0.5/1.5.

10 EXAMPLE 5

Using the procedure described in Example 1, 15ml of SiCl_4 were refluxed with zeolite produced from Example 1 (Sample Nos. CS0.10/58 + CS0.20/58 + CS0.10/76) at 57°C for 30 minutes. Four cycles were carried out.

15 The results are given in Table V below.

TABLE V

Sample No.	Reflux Cycle	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
20	S 1	2.09	2.04	33.4	1056
	SS 2	2.00	1.81	30.6	1063
	SSS 3	1.83	1.66	27.8	1078
	SSSS 4	1.81	1.62	27.4	1073
Starting material dealuminated zeolite				49.6	

Table VI reports the results of infra-red characterisation studies and Table VII the results of X-ray diffraction studies, confirming the increase of the Si/Al ratio of the zeolite Y framework.

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10

15

TABLE VI

Sample No.	Al/u.c.	Asymmetric (cm^{-1})	Symmetric (cm^{-1})	Double Rings (cm^{-1})
NaY	56.1	1015 s	790 m	582 m
CS (1)	50.1	1023 s	793 m	584 m
CS (4)	48.1	1030 s	793 m	585 m
CS0.33/58	46.8	1030 s	798 m	588 m
CS0.33/76	45.3	1030 s	800 m	588 m
S	33.4	1042 s	805 m	593 m
SS	30.6	1045 s	810 m	597 m
SSSS	27.4	1050 s	810 m	597 m

s = strong

m = medium

20

25

30

TABLE VII

Sample No.	Lattice Constant $a_0 + 0.06 \text{ \AA}$	Al/u.c.
NaY	24.59	36.1
SO.50/57	24.68	37.5
SI.0/57	24.48	37.0
SI.5/57	24.48	37.3
SS0.5/1.5	24.41	33.2
S	24.41	33.4
SS	24.41	30.6
SSS	24.38	27.8
SSSS	24.38	27.4
CS0.33/57	24.53	46.8
CS0.77/57	24.53	47.3

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EXAMPLE 6

Table VIII below reports the products (in sodium form) resulting from the dealumination of sodium Y zeolites by SiCl_4 in the solvent tetraethoxysilane $[(\text{C}_2\text{H}_5\text{O})_4\text{Si}]$ (TES). The
5 methods used were as follows:

Method A (Sample STES NaY)

About 1 gram of sodium Y zeolite [ZY(H)] was calcined at 600°C and allowed to cool in a desiccator. 25ml of TES were added to the zeolite followed by 1ml of SiCl_4 . The mixture was
10 refluxed for one hour.

Method B (Sample STES DY)

The method was as described under Method A above but sodium Y zeolite [ZY(D)] was used.

Method C (Samples STES DY 0.5; STES DY1; STES DY2 and STES DY18B)

15 About 19 grams of sodium Y zeolite (ZY[D]) was calcined at 600°C and allowed to cool in a desiccator. 45 ml of SiCl_4 were added to the zeolite with constant stirring for 1-2 minutes followed by 70ml of TES. The resultant slurry was refluxed for 18 hours. Zeolite slurry samples were withdrawn after 30 minutes,
20 one hour, two hour and 18 hour intervals.

From the results reported in Table VIII below, particularly the results of Method C, it can be seen that dealumination is substantially complete within the first 30 minutes of reaction time. These samples all showed very good crystallinity; as good
25 as the starting sodium Y zeolite.

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TABLE VIII

Sample No.	Reflux T°C	H ₂ O %	Al mmol/g	²² Na mmol/g	Si/Al ratio
1STES NaY	110-116	22.76	3.02	3.17	2.87
1STES DY	103	22.92	3.02	3.07	2.88
STES DY 0.5	80	21.15	2.28	2.07	4.43
STES DY 1	78	21.28	2.28	2.09	4.41
STES DY 2	78	20.89	2.46	2.05	4.05
STES DY 18B	78	21.32	2.28	2.07	4.41

TABLE VIII (continued)

Sample No.	Al/u.c.	Collapse T°C	Lattice Constant Å
1STES NaY	49.6	991	-
1STES DY	49.5	999	-
STES DY 0.5	35.4	1052	24.34
STES DY 1	35.5	1052	24.36
STES DY 2	38.0	1050	-
STES DY 18B	35.5	1010	24.36

EXAMPLE 7

Table IX reports the product (in sodium form) resulting from the dealumination of sodium Y zeolite by a SiCl₄/CCl₄/C₂H₅OH solvent mixture.

About one gram of sodium Y zeolite [56Al/u.c., ZY(H)] was calcined at 600°C for a few hours and allowed to cool in a desiccator. 12.5ml of CCl₄ were added to the zeolite followed by 1ml of SiCl₄. The mixture was refluxed at 56°C for 30

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minutes when 12.5ml of ethanol were introduced. Refluxing at 63°C was continued for a further 30 minutes.

TABLE IX

	Sample No.	1 CSEtNaY
5	Reflux	56/63°C
	H ₂ O	22.12%
	Al	2.9mmol/g
	²² Na	2.97mmol/g
	Si/Al ratio	3.04
10	Al/u.c.	47.5
	Collapse	994°C

EXAMPLE 8

Table X below reports the products (in sodium form) resulting from the dealumination of sodium Y zeolites by SiCl₄/ethanol solutions.

TABLE X

	Sample No.	Reflux T°C	H ₂ O %	Al mmol/g	²² Na mmol/g	Si/Al ratio
	SEtDY 0.5	70	22.41	2.72	2.68	3.39
20	SEtDY 1	70	22.46	2.71	2.69	3.40
	SO.5EtDY 0.5	70	22.21	2.60	2.60	3.62
	SO.5EtDY 1	70	22.47	2.62	2.48	3.58
	5S5EtDY	78.9	21.73	2.76	2.78	3.35
	10S10EtDY	78.3	22.09	2.81	2.79	3.25
25	1CSEt5NaY	75.2	22.34	2.79	2.65	3.29
	SEtNaY	57/74	19.79	2.81	2.80	3.39
	1SEtNaY	57/74	23.24	2.88	2.87	3.07
	SEtG	57/74	21.31	2.65	2.49	3.60

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TABLE X (continued)

Sample No.	Al/u.c.	Collapse $T^{\circ}\text{C}$
5	SEtDY 0.5	43.7
	SEtDY 1	43.6
	SO.5EtDY 0.5	41.6
	SO.5EtDY 1	41.9
	SSSEtDY	44.1
10	10S10EtDY	45.2
	1CSEt5NaY	44.8
	SEtNaY	43.7
	1SEtNaY	47.2
	SEtG	41.7

EXAMPLE 915 Method (i) (Samples SEtDY 0.5 and SEtDY 1)

20 About 5 grams of the sodium form Y zeolite (approximately 56 Al/u.c.; ZY[D]) was calcined at 600°C for a few hours and allowed to cool in a desiccator. 20 ml of SiCl_4 were added to the zeolite and stirred for 5 minutes. Five successive portions of CCl_4 of approximately 20ml were added to the zeolite slurry and the CCl_4 was discarded after centrifuging the slurry. 80ml of ethanol were then added and refluxed for one hour. Approximately 50ml of the slurry was withdrawn after 30 minutes and the rest after one hour.

25 Method (ii) (Samples SO.5EtDY0.5 and SO.5EtDY 1)

The method was the same as Method (i) above except that the

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contact time of the zeolite and SiCl_4 was increased to 15 minutes.

Method (iii) (Sample 5SSEtDY)

5 About 5 grams of sodium Y zeolite (ZY[D]) was calcined at 600°C for a few hours and cooled in a desiccator. 5ml of SiCl_4 were added to the zeolite and stirred for 5 minutes. 50ml of ethanol were then added to the slurry and refluxed for one hour.

Method (iv) (Sample 10S10EtDY)

10 The method was the same as Method (iii) above except that 10ml of SiCl_4 were used and the SiCl_4 -zeolite contact time was increased to 10 minutes.

Method (v) (Sample 1CSEt5NaY)

15 About one gram of sodium Y zeolite (ZY[H]) was calcined at 600°C for a few hours and allowed to cool in a desiccator. About 1ml of SiCl_4 was added to the zeolite and stirred for 5 minutes. 25ml of ethanol were then added to the slurry and refluxed for one hour.

Method (vi) (Sample SEtNaY)

20 About one gram of sodium Y zeolite (ZY[H]) was calcined at 600°C for a few hours and allowed to cool in a desiccator. About 15ml of SiCl_4 were added to the zeolite and refluxed for 30 minutes. The zeolite slurry was then centrifiged to separate the solid and liquid phases. The zeolite was washed with three
25 successive 10ml portions of CCl_4 . About 25ml of ethanol were added to the zeolite and refluxed for 15 minutes.

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Method (vii) (Sample 1SEtNaY)

The method was the same as Method (vi) except that 1ml of SiCl_4 and 14ml of CCl_4 were used in the first reflux.

Method (viii) (Sample SEtG)

- 5 The method was the same as Method (vi) except that 10 grams of sodium Y zeolite (ZY[G]), 80ml of SiCl_4 and 100ml of ethanol were used.

EXAMPLE 10

- 10 Table XI below reports the products resulting from the dealumination of sodium Y zeolites followed by treatment with various mixtures including SiCl_4 as a component.

TABLE XI

Sample No.	Temperature °C		H ₂ O %	Al mmol/g	²² Na mmol/g	Si/Al ratio	
	Preheat	Reflux					
15	<u>Method I - CSH SERIES</u>						
	CS4	100	59	24.30	2.90	3.01	2.97
				24.73	2.42	2.47	3.80
	CSH48	100	59	24.74	2.21	2.20	4.31
	CSH40	100	59	23.73	1.97	1.98	5.08
20	CSH32	100	59	24.96	1.56	1.56	6.64
	CSH24	100	59	23.99	1.22	1.23	9.00
	CSH16	100	59				
	<u>Method II - HCS SERIES</u>						
	HCS32	100	59	18.67	2.11	2.12	5.05
				17.52	1.25	1.27	9.61
	HCS16	100	59				

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Method III - STES SERIES

	STES NaY	300	71	21.78	2.96	3.05	3.02
	STES H48	300	71	21.58	2.66	2.76	3.53
	STES H40	300	69	20.24	2.44	2.51	4.07
5	STES H32	120	69	16.64	2.19	2.21	4.97
	STES H24	120	67	17.27	1.74	1.88	6.52
	STES H16	120	69	16.05	1.38	1.45	8.74

TABLE XI (continued)

	Sample	Al/u.c.	Collapse
10	No.		T°C

Method I - CSH SERIES

	CS4	48.4	1008
	CSH48	40.0	1021
	CSH40	36.2	1031
15	CSH32	31.6	1023
	CSH24	25.1	981
	CSH16	19.2	990

Method II - HCS SERIES

	HCS32	31.7	1021
20	HCS16	18.1	1014

Method III - STES SERIES

	STES NaY	47.8	993
	STES H48	42.4	1001
	STES H40	37.9	1013
25	STES H32	32.2	991
	STES H24	25.5	949
	STES H16	19.7	931

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5 The dealuminated zeolite is made by treatment of sodium Y zeolite with hydrochloric acid. Dealumination does not occur when the pH of the acid is greater than 2.30, while complete dealumination occurs at pH less than 0.46. It appears that four hydrogen atoms are required to remove one aluminium atom. This acid dealumination results in a structure which is less crystalline than the initial zeolite (due to accumulated defects in the structure) and is not thermally stable. However, treatment with SiCl_4 -containing mixtures allows insertion of silicon into the zeolite matrix and gives a product of reasonable thermal stability.

10 The treatment with SiCl_4 was by three different methods.

Method I - CSH SERIES

15 About 0.5 gram of dealuminated Y zeolite (by HCl treatment) in sodium form was dehydrated in an oven at 100°C for a few hours and then allowed to cool in a desiccator. The zeolite was then mixed with 15ml of CCl_4 followed by 0.30ml of SiCl_4 and refluxed for 30 minutes.

Method II - HCS SERIES

20 The procedure was the same as Method I above except that 10ml of CCl_4 and 5ml of SiCl_4 were used.

Method III - STES SERIES

25 About one gram of dealuminated Y zeolite (by HCl treatment) in sodium form (as used in Methods I and II above) was dehydrated in an oven at two temperatures (120°C and 300°C) for a few hours and then allowed to cool in a desiccator. The zeolite was

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then mixed with 3ml of SiCl_4 with constant stirring for 5 minutes. 20ml of TES was added to the slurry and refluxed for one hour. The highly dealuminated samples (those with fewer than 32 atoms of aluminium per unit cell) had poor crystallinity.

CLAIMS

1. A method for the modification of the framework structure of a zeolite, comprising treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework.
2. A method as claimed in claim 1, in which the aluminium-replacing element is selected from boron, tin, silicon, titanium, germanium, gallium, phosphorus, beryllium aluminium and magnesium.
3. A method as claimed in claim 1 or claim 2, in which the said compound is selected from the halides of the aluminium-replacing element.
4. A method as claimed in claim 3, in which the halide is selected from BCl_3 , BBr_3 , SnCl_4 , SnBr_4 , SnI_4 , SiCl_4 , SiI_4 , TiCl_4 , GeCl_4 , GaCl_3 , PCl_5 , BeCl_2 , AlCl_3 and MgCl_2 .
5. A method as claimed in claim 4, in which the halide is silicon tetrachloride.
6. A method as claimed in claim 1 or claim 2, in which the said compound is an organometallic compound.

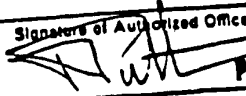
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7. A method as claimed in claim 6, in which the organometallic compound is beryllium diphenyl.
8. A method as claimed in any preceding claim, in which the organic solvent is carbon tetrachloride or ethanol or a mixture thereof.
9. A method as claimed in any of claims 1 to 7, in which the solvent is an organic liquid having molecules which are too large to enter the channels of the zeolite.
10. A method as claimed in claim 9, in which the solvent is tetraethoxysilane.
11. A method as claimed in any preceding claim, in which the zeolite is selected from Erionite, Beta, ZSM-5, ZSM-11, Mordenite, Chabazite, and Offretite.
12. A method as claimed in any preceding claim, in which the treatment carried out under solvent reflux conditions.
13. A method as claimed in any preceding claim, in which the zeolite is pretreated with acid to remove aluminium therefrom.
14. A method of thermally cracking petroleum hydrocarbons characterised in that said cracking is conducted in the presence of a modified zeolite; said zeolite being the product of a process as claimed in any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 87/00591

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁴ : C 01 B 33/28; C 01 B 35/10; B 01 J 29/04; C 10 G 11/05		
II. FIELDS SEARCHED Minimum Documentation Searched ⁷ Classification System Classification Symbols IPC ⁴ . B 01 J 29/00 Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	GB, A, 1332468 (UNION CARBIDE) 3 October 1973, see page 3, lines 99-130	
A	US, A, 3528768 (S. TUCKER) 15 September 1970	
A	EP, A, 0012570 (MOBIL OIL) 25 June 1980, see pages 17-22	
A	EP, A, 0037630 (MOBIL OIL) 14 October 1981, see pages 21-24	
A	EP, A, 0050907 (MOBIL OIL) 5 May 1982, see pages 14-15	
A	EP, A, 0040900 (MOBIL OIL) 2 December 1981, see pages 20-21	
A	EP, A, 0034918 (MOBIL OIL) 2 September 1981, see pages 20-21	

¹⁴ Special categories of cited documents: ¹⁵ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
IV. CERTIFICATION Date of the Actual Completion of the International Search 8th December 1987 International Searching Authority EUROPEAN PATENT OFFICE		Date of Mailing of this International Search Report 25 JAN 1988 Signature of Authorized Officer  P.C.G. VAN DER PUTTEN

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